

PATENT SPECIFICATION

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NO DRAWINGS

1 242 320

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(23) Complete Specification filed 28 Jan. 1970
(45) Complete Specification published 11 Aug. 1971
(51) International Classification C 07 c 51/56
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ERRATA

SPECIFICATION NO 1242320

Page 3, line 45, *for* ~~excesisvely~~ *read* excessively

Page 3, line 92, *for* ~~excelent~~ *read* excellent

Page 3, line 117, *for* ~~converqsion~~ *read* concentration

Page 3, line 119, *for* ~~concentration~~ *read* conversion

Page 5, line 3, *for* ~~0-01%~~ *read* 0-0.1%

Page 5, line 97, *for* ~~proceding~~ *read* preceding

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ERRATUM

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Page 1, Heading, Application Filed (22) *for* '30 Jan 1968' *read* '30 Jan 1969'.

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28 February 1972

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condensation by cooling and, in practice, can consequently be recovered only by absorption in a solvent, which is generally water. In other words, in practically all processes actually used on an industrial scale, at least part of the anhydride will finally be recovered in the form of an aqueous solution of maleic acid.

All processes hitherto described for the dehydration of maleic acid to maleic anhydride encounter various practical difficulties, which obviously vary from one process to another. A difficulty which is not overcome in any known process results from the inevitable presence of two types of impurities, one being due to the presence of intermediate products of the oxidation of benzene to maleic anhydride and the other being due to impurities, particularly fumaric acid, formed in the course of the dehydration of the maleic acid solution.

A disadvantage of the process using selective solvents is, first, the danger of fire and intoxication, the inevitable losses of solvents in the course of their recycling and the poor calorific efficiency due to their low specific heat compared with that of the water to be evaporated and, secondly, the obligatory periodic stopping of the installation in order to eliminate the deposits of fumaric acid which are formed in the course of time.

Among the processes in which part of the maleic anhydride is recovered in the form of an aqueous solution of maleic acid, some processes previously effect partial or complete elimination of the water of dissolution and then introduce the maleic acid, partly or completely dehydrated in this manner, into a considerable mass of boiling maleic anhydride, so as to obtain a vaporised mixture containing maleic anhydride and water, which is then subjected to con-

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and slip number 2

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(54) PROCESS FOR THE DEHYDRATION OF MALEIC ACID

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Bruxelles, Belgium, a Body Corporate or-
ganised under the laws of Belgium, do
hereby declare the invention, for which we
pray that a patent may be granted to us,
and the method by which it is to be per-
formed to be particularly described in and
by the following statement:—

The present invention is concerned with
a continuous process for the dehydration of
maleic acid to form maleic anhydride and,
more particularly, with the recovery of
maleic anhydride from a maleic acid solu-
tion obtained in the continuous production
of maleic anhydride by the catalytic oxida-
tion of hydrocarbons, particularly benzene.

In the gaseous effluent of the reactor, the
maleic anhydride vapours are highly diluted
with a mixture of inert gases, such as nitro-
gen and unconsumed oxygen. Although the
vapour pressure of the maleic anhydride
amounts to only a few mm. mercury at the
melting temperature of the product, the
dilution is such that at least 15% of the
anhydride leaving the reactor evades con-
densation by cooling and, in practice, can
consequently be recovered only by absorp-
tion in a solvent, which is generally water.
In other words, in practically all processes
actually used on an industrial scale, at least
part of the anhydride will finally be re-
covered in the form of an aqueous solution
of maleic acid.

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of impurities, one being due to the presence
of intermediate products of the oxidation
of benzene to maleic anhydride and the
other being due to impurities, particularly
fumaric acid, formed in the course of the
dehydration of the maleic acid solution.

These two types of impurities are invari-
ably concentrated either in all the maleic
anhydride produced or in only part of the
latter; in either case, the problem arises of
separating these impurities from the maleic
anhydride entraining them. This operation
is delicate and, in addition, inevitably en-
tails quite considerable losses of maleic an-
hydride. In fact, these impurities retain a
not inconsiderable amount of maleic anhy-
dride. In processes employing extraction
by distillation, there are additional losses
due to the decomposition and isomerisation
which accompany this operation.

At the present time, the most usual pro-
cess for the recovery of maleic anhydride
consists in subjecting the reactor effluent to
partial condensation at a temperature
higher than the dewpoint of water vapour,
in order to recover part of the maleic an-
hydride directly, and then washing the gas-
eous effluent either with solvents which
selectively absorb the residual maleic an-
hydride or with water, with simultaneous
conversion of the anhydride into maleic
acid.

A disadvantage of the process using
selective solvents is, first, the danger of fire
and intoxication, the inevitable losses of
solvents in the course of their recycling and
the poor calorific efficiency due to their low
specific heat compared with that of the
water to be evaporated and, secondly, the
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tion in order to eliminate the deposits of
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of time.

Among the processes in which part of
the maleic anhydride is recovered in the
form of an aqueous solution of maleic acid,
some processes previously effect partial or
complete elimination of the water of dis-
solution and then introduce the maleic acid,
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manner, into a considerable mass of boiling
maleic anhydride, so as to obtain a vapor-
ised mixture containing maleic anhydride
and water, which is then subjected to con-

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densation, which may or may not be fractional, at a temperature higher than the dewpoint of the water vapour present in the system. According to the inventors of this known process, the quality of the maleic anhydride which can thus be obtained is generally excellent; nevertheless, it is a disadvantage that the calorific energy and operating power requirements for constantly maintaining the maleic anhydride mass in circulation at a high temperature are considerable; furthermore, at high temperatures, not inconsiderable amounts of fumaric acid are formed and accumulate in the evaporator and these have to be removed periodically, thus entailing a non-continuous operation of the installation.

In other processes for the recovery of the residual anhydride in the form of an aqueous solution of maleic acid, direct conversion of the acid into anhydride is effected without making use of a heated mass of circulating maleic anhydride. It is obvious that this technique is much less expensive than that described above; however, this direct conversion is delicate because it is necessary to heat the reaction mixture to a high temperature, at which partial isomerisation of the maleic acid into fumaric acid inevitably occurs, which not only constitutes a loss of output but also involves a risk of obstructing the installation. Furthermore, up to the present time, no means have yet been found for continuously eliminating the contaminants from the system, for example traces of catalysts, resins and the by-products which are formed either in the synthesis reactor and appear again in the aqueous absorption solution or are formed in the recovery installation, such as fumaric acid, without having to interrupt the continuous production for the purposes of cleaning, and while still obtaining a maleic anhydride product of great purity and practically free from maleic acid and/or fumaric acid.

It is the provision of a solution of this problem which constitutes the object of the present invention.

According to the present invention, maleic anhydride is obtained, with a purity of at least 99% by weight and with a fumaric acid content of 0—0.1% by weight, when maleic anhydride is continuously obtained from a maleic acid solution by the application of a process characterised by the following operational steps:

(a) The maleic acid solution is heated in a concentration zone at a temperature of between 100 and 150°C. and at a pressure of between 400 and 760 mm. Hg. until the water content of the maleic acid is reduced to 0—10% by weight;

(b) The maleic acid obtained in stage (a) is treated in a conversion zone at a tem-

perature of between 150 and 200°C. and at a pressure of between 40 and 300 mm. Hg. until from 10 to 97%, advantageously 85 to 95%, and preferably about 90% by weight of the maleic acid is converted into maleic anhydride, to give a liquid phase of impure maleic acid and a purified gaseous phase containing maleic anhydride and water vapour;

(c) The impure liquid phase produced in stage (b) is treated with an aqueous solution of maleic acid in a dissolution and filtration zone to provide a solid residue containing the impurities and any fumaric acid which may have been formed, which is removed from the system, and a filtrate consisting of an aqueous solution of purified maleic acid, which is either recycled partly to stage (a) and partly to the impure liquid phase produced in stage (b) or which is removed from the system;

(d) In a condensation zone, the gaseous phase consisting of maleic anhydride and water vapour produced in stage (b) is condensed at a temperature higher than the dewpoint of the water vapour present in the gaseous phase and there is thus obtained maleic anhydride of the desired purity; the residual vapour is washed with water and the solution thus obtained containing maleic acid is optionally returned to stage (a).

The aqueous maleic acid solution used as starting material for the process according to the present invention is preferably that obtained by washing the effluent of a catalytic oxidation reactor for hydrocarbons, particularly benzene, after part of the maleic anhydride has been condensed. Nevertheless, according to a particularly advantageous embodiment of the present invention, it is also possible to retain all the maleic anhydride formed in the reactor, in the form of an aqueous solution of maleic acid, by washing with water, i.e. without partial condensation of maleic anhydride. This latter embodiment is very advantageous because it makes it possible to eliminate entirely the cost of investment necessary for maleic anhydride condensers, which normally represent 15 to 25% of the total investment costs for the maleic anhydride recovery installation.

Whatever the method of operation adopted, i.e. partial or total extraction with water of the maleic anhydride in the form of an aqueous solution of maleic acid, any concentrations of maleic acid in the aqueous solution thus obtained may be used for carrying out the process of the present invention; nevertheless, for economic reasons, it is obvious that this concentration should be as high as possible and that it will preferably be close to saturation concentration under the operating conditions used for the washing. Thus, as an indication, the con-

centration of maleic acid in the aqueous solution may be about 450 grams per litre but it is obvious that other concentrations may be used, without departing from the scope of the present invention.

The concentration zone referred to in (a) may be constituted by one or more evaporator apparatus of known type; however, preference is given to the so-called thin layer evaporators. In this concentration zone, the temperature is kept between 100 and 150°C., preferably at about 135°C. while the pressure is maintained between 400 and 760 mm.Hg., preferably at about 500 mm. Hg. until the water content of the maleic acid is reduced to 0—10% by weight. For the good performance of the process it is advantageous to lower the water content of the solution to as low a value as possible. The residence time of the maleic acid in the concentration zone is advantageously from 0.1 to 5 minutes, preferably less than 1 minute. The partially or completely dehydrated maleic acid at the outlet of the concentration zone is in the form of a liquid and its temperature is between 125 and 150°C. Because of the mild operating conditions applied in the concentration zone and of the short residence time, the presence of fumaric acid in the maleic acid obtained in this manner is practically undetectable.

The resulting hot maleic acid is passed to a conversion zone, which may be constituted by one or more evaporators of known type but preferably of the so-called thin layer type. In this conversion zone, the operating conditions are more severe than in the concentration zone, so as to permit elimination of the water of constitution from the maleic acid and thus to convert the acid into maleic anhydride. Nevertheless, as has been mentioned above, there is a danger of the formation of fumaric acid when maleic acid is heated at excessively high temperatures. For this reason, according to the present invention, sufficiently moderate operating conditions are adopted for the conversion zone in order to ensure that the maleic acid is only partly converted into maleic anhydride and, in addition, the operation is so conducted as to be able to separate in this zone not only the fumaric acid which may be formed in the course of the conversion but also all the impurities which accompany the maleic acid, i.e. traces of secondary products originating from the catalytic oxidation reactor, particularly resinous products and benzoquinone. For this purpose, the conversion of maleic acid in this zone is effected at a temperature of between 150 and 200°C. and at a pressure of between 40 and 300 mm. Hg., until from 10 to 97%, advantageously from 85 to 95% and preferably about 90% by weight of the maleic acid is converted

into maleic anhydride, thus forming a liquid phase of maleic acid containing the above-mentioned impurities and any fumaric acid formed, which is continuously eliminated at the bottom of the conversion zone, and a purified gaseous phase containing maleic anhydride and water vapour, which leaves the conversion zone at the top. In order to avoid excessive formation of fumaric acid, which, even if it does not contaminate the maleic anhydride, since it is eliminated with the unconverted maleic acid, nevertheless constitutes an irrecoverable loss of output, the residence time of the material in the conversion zone is as short as possible and is generally less than 1 minute.

As indicated above, it would be possible to convert only 10% of the maleic acid into maleic anhydride, while, nonetheless, obtaining the advantageous effects of the process of the present invention. It will, however, be understood that, from the point of view of thermal and economic balances, the amount of maleic acid unconverted should be reduced to the minimum. Pilot plant scale tests have shown that it is possible to obtain a maleic anhydride of excellent quality, with a purity higher than 99% by weight and containing from 0 to 0.1% by weight of fumaric acid, when the content of unconverted maleic acid in the conversion zone amounts to about 10% by weight. Finally, if it is desired to do so, it is also possible to effect the conversion of maleic acid into its anhydride in the conversion zone in the presence of known dehydration catalysts, although this step is by no means necessary in order to obtain the advantages of the process of the present invention.

The impure liquid phase, which contains the impurities present in the original aqueous solution of maleic acid or formed in the course of the conversion of the maleic acid into its anhydride in the conversion zone, including any fumaric acid formed, is withdrawn continuously at the bottom of the conversion zone and passed to a dissolution and filtration zone, in which the solid impurities are separated in the form of a filter cake from a liquid filtrate constituted by purified aqueous maleic acid, which may be recycled partly to the conversion zone and partly to the impure liquid phase produced in the concentration zone. However, it is also possible to withdraw the purified aqueous solution of maleic acid from the system, for example in order to use it as raw material for another synthesis.

The purified gaseous phase containing maleic anhydride and water vapour and produced in the conversion zone, is passed into a condensation zone in which, on the one hand, the maleic anhydride is condensed at a temperature above the dewpoint of the water vapour contained in this phase and,

on the other hand, the uncondensed portion of the gaseous phase is washed with water in order to recover, in the form of an aqueous solution of maleic acid, the maleic anhydride which remains in the uncondensed portion. The maleic anhydride condensed in the aforesaid condensation zone constitutes the product of the present process; its purity amounts to at least 99% by weight and its fumaric acid content is from 0 to 0.1% by weight. Nevertheless, in order to impart to it the degrees of purity and stability imposed by commercial standards, this product can easily be treated by suitable, wellknown methods, particularly by vacuum distillation. The aqueous solution of maleic acid obtained by washing the gaseous phase may be recycled to the top of the concentration zone.

In the process according to the present invention, the yield of maleic anhydride obtained from the maleic acid solution used as starting material is very high, since it attains at least 98—99% by weight of theoretical yield.

The following Example is given for the purpose of illustrating the present invention, reference being made to the drawing accompanying the provisional specification, which shows a flow diagram of the process:—
Example

Referring to the drawing accompanying the provisional specification an aqueous solution of 450 g./litre maleic acid originating from a washer (not illustrated) installed at the outlet of a reactor for the catalytic oxidation of benzene (not illustrated) is fed at the rate of 1000 moles per hour through a pipe 10 to the top of a thin layer evaporator 1. These 1000 moles per hour of maleic acid are made up of 900 moles per hour of aqueous maleic acid coming from the washer (not illustrated) through a pipe 12 and 100 moles per hour of maleic acid coming from a mixing zone 6 and filtration zone 8 and through a pipe 11.

The water vaporised from the aqueous solution of maleic acid at a temperature of 135°C. and at a pressure of 550 mm.Hg. in the evaporator 1 escapes through a pipe 13 and is condensed in the barometric washer 2 connected to a vacuum source (not illustrated), while the maleic acid, which now only contains about 1% by weight of water, leaves at the bottom of the evaporator 1 at a temperature of 135°C. and is passed through a pipe 14 to the top of a second thin layer evaporator 3.

In the evaporator 3, in which the melted maleic acid is gradually brought to a temperature of 200°C. at a pressure of 150 mm.Hg., the maleic acid is converted, to an extent of 90% by weight, into maleic anhydride in the form of a vaporised mixture

of maleic anhydride and water, while the remaining 10% of unconverted maleic acid flows off in the form of a liquid phase to the bottom of the evaporator 3.

The water vapour and maleic anhydride vapour are passed through a pipe 15 into a condenser 4 operating at a temperature of 80°C. The maleic anhydride obtained as product of the process is collected in the liquid state at the base of the condenser 4 at the rate of 900 moles per hour; its maleic anhydride content is 99.5% by weight, its content of fumaric acid is practically nil and its content of other impurities amounts to 0.4% by weight. If necessary, the maleic anhydride thus obtained is passed into a distilling column (not shown), in order to be freed from the last traces of impurities, and is stabilised. The water vapour which escapes at the top of the condenser 4 is passed through a pipe 16 to a barometric washer 5 connected to a vacuum source (not shown), in order to recover traces of maleic anhydride entrained by the water vapour; the resulting aqueous solution of maleic acid may be recycled (not illustrated).

The liquid phase of maleic acid, which flows off at the bottom of the evaporator 3 and which contains, in suspension, all the impurities accumulated in the installation, is mixed with a part of the maleic acid solution circulating in the cycle 6, 20, 7, 21, 8, 11, 17, 3 and is collected in a receiver 6. This receiver operates at a temperature of 30°C. and at a pressure of 40—300 mm.Hg. The solution is withdrawn from 6 through a pipe 20 by means of a pump 7 and delivered through a pipe 21 to a filter 8. The filter 8 is designed so as not to interrupt the continuous operation of the installation (double filtration circuit, not illustrated). The filter cake, which contains the impurities accumulated in the system (including fumaric acid and various impurities originating from secondary reactions on the catalyst), is eliminated from the installation, while the filtrate, composed of an aqueous solution of maleic acid, leaves the filter through the pipe 11 and is mixed with a fresh solution of maleic acid to be treated, arriving through pipe 12.

The process according to the present invention is, therefore, very clearly distinguished from all previously known processes by the fact that it makes it possible: 1). to convert maleic acid directly into maleic anhydride and to separate the impurities, without the latter being mixed with the maleic anhydride, because they are entrained by the fused maleic acid; 2). to eliminate the impurities continuously and practically without loss of anhydride or of maleic acid.

The advantages offered by the process of the present invention are numerous:

- a) A maleic anhydride is obtained, the purity of which is at least 99% by weight, with a fumaric acid content of 0—0.1% by weight.
- 5 b) The yield of maleic anhydride is very high and attains from 98% by weight to more than 99% by weight of the theoretical value.
- 10 c) The impurities are eliminated from the installation continuously, without ever having to stop the installation for cleaning purposes, as is the case with previously known installations.
- 15 d) Because of the almost theoretical yield of the process, it is possible to eliminate the condensers which are generally installed at the outlet of the reactor, in order to condense the maleic anhydride direct from the effluent, which represents a saving of about 20 15—25% of the total investment costs.
- e) The operation of the installation is flexible, in that the operating conditions can be modified in accordance with the initial degree of purity of the maleic acid solution to be treated.
- 25 f) Unlike certain known processes, it is not necessary to keep in circulation a considerable heated mass of maleic anhydride; the economy of the process is, therefore, improved, the danger of formation of fumaric acid is reduced to a minimum and the yield of the operation of recovery of maleic anhydride is increased accordingly.
- tem, and a filtrate consisting of an aqueous solution of purified maleic acid, which is either recycled partly to stage (a) and partly to the impure liquid phase produced in stage (b) or is removed from the system;
- (d) condensing in a condensation zone the gaseous phase consisting of maleic anhydride and water vapour produced in stage (b) at a temperature higher than the dewpoint of the water vapour present in the gaseous phase, thus obtaining maleic anhydride of the desired purity; washing the residual vapour with water and returning, if desired, to stage (a) the solution thus obtained containing maleic acid.
2. Continuous process according to claim 1, wherein the maleic acid solution of stage (a) is heated in the concentration zone at a temperature of about 135°C.
3. Continuous process according to claim 1 or 2, wherein the maleic acid solution of stage (a) is heated at a pressure of about 500 mm.Hg.
4. Continuous process according to any of the preceding claims, wherein the conversion of maleic acid to maleic anhydride in stage (b) is 85—95% by weight.
5. Continuous process according to claim 4, wherein the conversion of maleic acid to maleic anhydride in stage (b) is about 90% by weight.
6. Continuous process according to any of the preceding claims, wherein the maleic acid solution used as starting material is obtained by washing the effluent of a catalytic oxidation reactor for hydrocarbons, after part of the maleic anhydride has been condensed.
7. Continuous process according to any of claims 1 — 5, wherein the maleic acid solution used as starting material is obtained by washing the effluent of a catalytic oxidation reactor for hydrocarbons, without previous condensation of maleic anhydride.
8. Continuous process according to claim 6 or 7, wherein the maleic acid solution used as starting material is obtained by washing the effluent of a catalytic oxidation reactor for benzene.
9. Continuous process according to any of the preceding claims, wherein the concentration zone of stage (a) is constituted by at least one thin layer evaporator.
10. Continuous process according to any of the preceding claims, wherein the conversion zone of stage (b) is constituted by at least one thin layer evaporator.
11. Continuous process according to any of the preceding claims, wherein the maleic anhydride obtained as the product of the process at stage (d) is subjected to vacuum distillation.
12. Continuous process according to

WHAT WE CLAIM IS:—

1. Continuous process for the production of maleic anhydride of at least 99% by weight purity and containing 0—0.1% by weight of fumaric acid from an aqueous solution of maleic acid, which comprises
- (a) heating the maleic acid solution in a concentration zone at a temperature of between 100 and 150°C. and at a pressure of between 400 and 760 mm.Hg. until the water content of the maleic acid is reduced to 0—10% by weight;
- (b) treating the maleic acid obtained in stage (a) in a conversion zone at a temperature of between 150 and 200°C. and at a pressure of between 40 and 300 mm.Hg. until from 10 to 97% by weight of the maleic acid is converted into maleic anhydride, to give a liquid phase of impure maleic acid and a purified gaseous phase containing maleic anhydride and water vapour;
- (c) treating the impure liquid phase produced in stage (b) with an aqueous solution of maleic acid in a dissolution and filtration zone to provide a solid residue containing the impurities and any fumaric acid which may have been formed, which is removed from the sys-

claim 1 for the production of maleic anhydride, substantially as hereinbefore described and exemplified.

13. Maleic anhydride, whenever produced by the process according to any of claims 1—12.

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